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ANALYSIS OF STM TOPOGRAPHS OF GRAPHITE SURFACES ROUGHENED BY Ar^+ ION BOMBARDMENT

by

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ANALYSIS OF SCANNING TUNNELING MICROSCOPE TOPOGRAPHS OF GRAPHITE SURFACES ROUGHENED BY Ar^+ ION BOMBARDMENT

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ABSTRACT

The scanning tunneling microscope (STM) has been used to investigate graphite surfaces roughened by 5 keV Ar^+ ion bombardment. The (0001) surfaces of several samples were etched with the same total ion dose but with different sputter rates for each surface. STM images taken after sputtering show that the roughness of the sputtered surfaces depended on the sputter rate and that the surface topography of each sample appeared self-similar over a large range of length scales. These experimental observations agree with predictions of the recently proposed Shadow Model. The two dimensional height-height correlation function is utilized as a means of quantitative analysis for STM topographs of sputtered surfaces.

INTRODUCTION

Ion beam sputter etching (IBSE) is widely used to prepare surfaces for processing or analysis by stripping off the outermost layers of the sample.[1,2] Controlling the topography of the resulting surfaces is important, but the dependence of the resulting surface morphology on the bombardment conditions is not well known.[3] For example, there is still much debate on the origin and evolution of cone-like features seen on surfaces prepared by IBSE.[4,5] The lack of quantitative predictive power regarding topology of bombarded surfaces is a major problem in surface science.

The scanning tunneling microscope (STM)[6,7] has been used to investigate the microscopic surface topography of graphite surfaces before and after sputter etching. The STM results agree qualitatively with predictions of a recently proposed general theoretical model by Karunasiri, Bruinsma and Rudnick[8,9] for sputter growth and erosion of surfaces. Computer simulations[8,9] and the STM experiments presented here show both a dependence of the surface roughness on the etching rate, and that each sputtered surface is self-similar over a wide range of length scales.

It is, of course, important to somehow quantify the morphology of these roughened surfaces. This has been accomplished here by calculating the two dimensional height-height correlation function from STM topographs of sputter etched surfaces. This form of data compression is very useful when examining sputtered surfaces. The correlation function plots show that the surfaces are correlated and self-similar over a finite length scale. They can also be used to recognize anisotropy on these surfaces, which may be due to the sputtering conditions, and can be useful as a diagnostic for testing the symmetry of the STM scanning axes.

EXPERIMENTAL RESULTS AND DISCUSSION

The surface chosen for this investigation was the (0001) face of highly oriented pyrolytic graphite (HOPG), which is easily cleaved to produce large, atomically flat regions.[10] This cleaved surface is inert when exposed to air and is easily imaged with the STM, revealing atomic scale features.[10] In addition, graphite has a rigid lattice, as seen by its melting temperature of ≈3800°C. This indicates that surface diffusion effects should be small and that topographical features produced by the bombardment are 'frozen in' and can be observed with the STM long after the sputtering has taken place. In general, surface diffusion is an important effect, which tends to smooth out surface features, so materials that can anneal at ambient temperatures are unsuitable for the experiments described here.

The graphite samples were cleaved to expose fresh surfaces and then examined with the STM before sputter etching. The microscope was operated at atmospheric pressure, in both the constant height and constant current modes,[6,7] and all images were obtained without filtering or extensive data processing. The excellent image quality obtained without enhancement is due to the fact that our STM was designed and built to have especially high stability and to be very insensitive to vibrational noise and thermal drift. Images collected on the 25 x 25 $Å^2$ scale clearly show the familiar atomic scale features of graphite.[7,10] In this study, however, we are concerned with larger scale topology, which is also easily obtainable. Images of freshly cleaved graphite taken on larger scales (eg., 100 x 100 $Å^2$ to 500 x 500 $Å^2$) appear flat at the lower magnifications.

The graphite samples were sputtered with a large area, rastered beam of 5 keV Ar^+ ions in a Kratos surface treatment chamber (base pressure ≈ 2 x 10^{-9} Torr). The beam was incident at 30° from the surface normal. The first six samples all received a total dose of 2.6 x 10^{16} ions over a 9mm^2 area (2.9 x 10^{17} ions/cm^2). The only parameter varied in this series was the sputtering **rate**, which was adjusted by flowing Ar gas into the ion gun at different rates. These first six samples were etched with ion fluxes varying from 2.4 x 10^{13} ions/cm^2-sec to 8.9 x 10^{14} ions/cm^{2}sec, corresponding to beam currents in the range of 0.35 μA to 12.76 μA, with the exposure time adjusted to obtain the same total dose. One additional graphite sample was etched with a beam current of 5.7 μA and recieved a lower dose of 1.1 x 10^{17} ions/cm^2. These current and flux measurements are only approximate, since the current was collected from the sample without suppression of secondary electrons. In this study, however, only the relative values of the beam flux are important. With a crude estimate of one carbon atom ejected per incident Ar^+ ion,[11] the ion etching removed approximately 300 monolayers of material from each graphite surface. The resulting surfaces should be amorphous to the penetration depth of the incident ions (≈ 40 Å).[12]

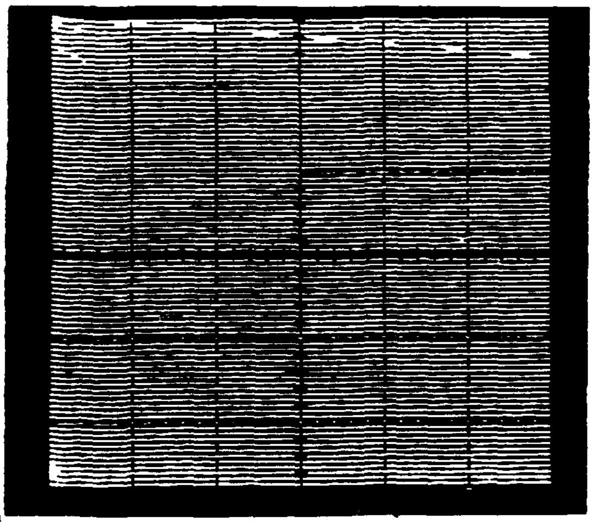
After etching, the first six graphite samples were re-examined with the STM using the same operating parameters present prior to sputtering. Six different length scales, ranging from 25 x 25 $Å^2$ to 500 x 500 $Å^2$, were used to investigate each of the samples. The constant height mode of imaging was used for most of the images presented here, primarily because the initial scans before sputtering were performed in this mode and also because it takes less time to acquire the data. While the tip will not be able to follow the rough topography exactly in this mode of imaging, the overall changes in surface roughness are clearly observable. Some additional constant current images[6,7] of these same surfaces were collected to confirm the topography seen in the constant height data and to make approximate measurements of the heights of the surface features. As a further check, several different STM sensitivity settings were tried on one of the samples. In this test, the shapes of the surface features changed somewhat as a function of instrument sensitivity but the same general trends in surface roughness were seen in the data and the surface features could be imaged through many consecutive scans, eliminating the possibilty that they were artifacts of the electronics. In addition, the features on the sputtered surfaces could be imaged reproducibly several days after the sputter etching, indicating minimal degradation of the surfaces with time.

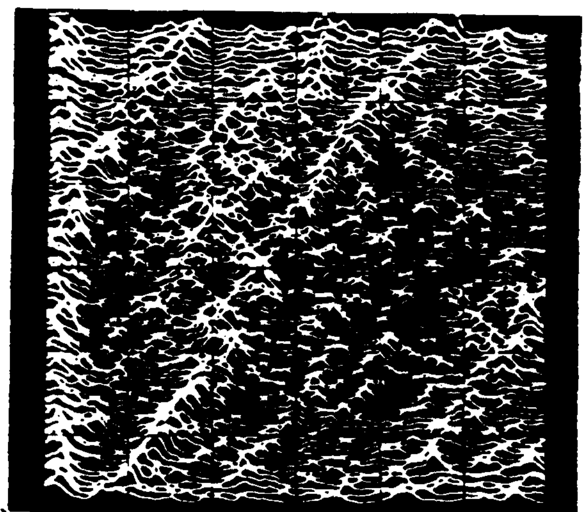
The once smooth graphite surfaces (Fig. 1(a)) were considerably roughened by the sputter etching on the distance scales measured with the STM (Figs. 1(b) and 1(c)). Constant current images of these first six sputtered samples (not shown) indicate that the surface features on the sputtered graphite are approximately 10 to 30 Å high. A comparison of Figs. 1(b) and 1(c) clearly shows that the roughness produced by sputtering is dependent on the sputter **rate**. For high rates, eg. Fig. 1(c), the surfaces are very rough, ie. they are characterized by a high density of features, while the lower beam fluxes, eg. Fig. 1(b), produced surfaces which were much smoother, with features that are less pronounced and at greater separations. This dependence of roughness on sputter rate was seen in five of the six ion etched samples studied with the constant height mode, each sample being sputtered at a different rate. Two samples were bombarded with nearly the same rate, and the STM images of the resulting surfaces were essentially identical at all length scales, showing the reproducibility of the sputter etching prodedure. While the differences in roughness between samples bombarded with different fluxes is most apparent in the 500 x 500 $Å^2$ images of Fig. 1, the same trends were seen clearly on all six length scales investigated. This is the first experimental report of sputter-rate dependent topography on these length scales.

The surface topography and the dependence of roughness on sputter rate observed in the experimental data agree qualitatively with computer simulations of etching using the newly proposed Shadow Model of sputter growth and erosion.[8] This model accounts for three effects: surface diffusion, differences in local surface exposure angle due to shadowing by surface features, and shot noise, a term which describes the statistical fluctuations in the number of incoming ions (or outgoing sputtered surface atoms). The shot noise term describes the effects of atomicity in the sputtering process.

The etching simulations show that after some time of sputtering, an initially smooth surface develops a rough mountain-like morphology.[9] In this case, surface diffusion should act to smooth out surface features, the shadowing effect initially has no effect (flat surface) and the shot noise should act to roughen the surface. In other words, the simulations predict that initially flat surfaces are unstable against shot noise during IBSE, exactly as seen in the experiments. The Shadow Model also predicts the observed dependence of roughness on etching rate, namely that at high ion fluxes features are produced on the surface at both short and long length scales. For a smaller erosion rate, the model predicts that the features at short length scales should be absent, as observed experimentally in Fig. 1.

Many experimental studies have shown that large cone-like structures are produced during the sputter etching process.[4] In some instances, it has been found that these features were caused by surface impurities which shield underlying substrate atoms from the incident sputtering particles.[5] These impurities may be intrinsic to the surface or may be introduced by the sputtering of atoms from the sample holder onto the sample.[13] The features observed in this study are much smaller than the above mentioned sputter cones and, furthermore, the dependence


(a)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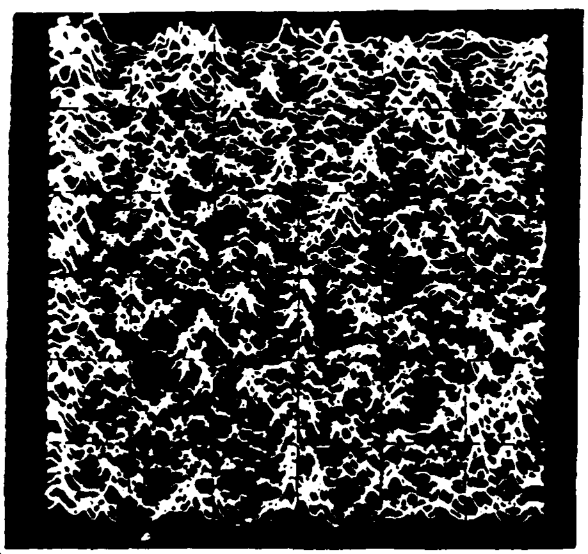
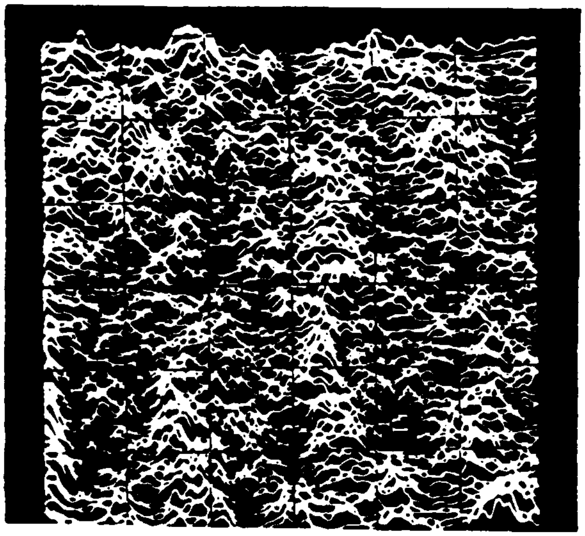

(c)

Fig. 1 Series of 500 x 500 Å^2 STM images of: (a) the surface of graphite before sputtering; (b) the graphite surface after sputter etching with 5 keV Ar^+ ions using a flux of 4.9 x 10^{13} ions/cm^2-sec (ion beam current of 0.7μA) for 100 min. ; (c) the graphite surface after sputtering with 5 keV Ar^+ ions using a flux of 8.8 x 10^{14} ions/cm^2-sec (beam current of 12.7μA) for 5.5 min.. The roughening produced by the removal of approximately 300 monolayers of material is seen clearly in (b) and (c). The difference in surface roughness between (b) and (c) is due entirely to the different sputtering rates used for these two samples. This trend was clearly evident on three other surfaces with intermediate etch rates. All images were collected using the same amplifier sensitivities, tunneling current (1.3 nA) and bias voltage (-37 mV).

on etching rate is not explained by the presence of impurities. It is possible, however, that the behavior observed on sputtered graphite is a combined effect of the shot noise inherent in the ion bombardment process and also of the impurities present. The features seen in the STM scans may represent the initial stages of sputter cone formation.

Another interesting property of surfaces produced by IBSE, microscopic self-similarity, can be seen in Fig. 2. This scaling behavior was seen on all sputtered graphite surfaces but was most apparent in those samples which were etched using the highest ion fluxes and therefore had the greatest roughness. The higher etch rates produced clearly self-similar surfaces over the range in length scales from 50 x 50 $Å^2$ to 500 x 500 $Å^2$, while on the surfaces sputtered at slow rates the self-similarity was observed only in the larger area scans, typically 100 x 100 $Å^2$ to 500 x 500 $Å^2$. Self-similarity is related to the process producing the surface and serves as a general way to classify different growth and erosion models. Computer simulations using the Shadow Model also produce self-similar surfaces.[8,9]

(a)


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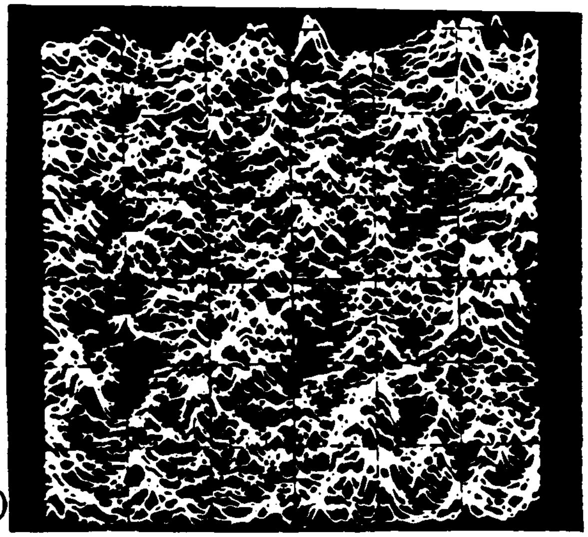

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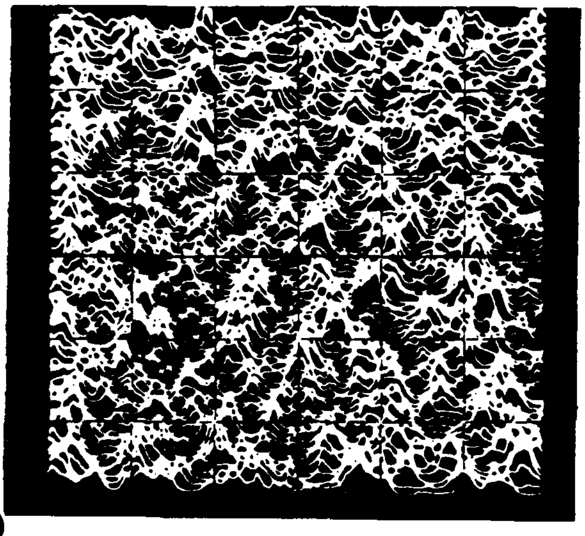

Fig. 2 STM images, collected at different magnifications, of the sputtered HOPG surface shown in Fig. 1(c). The scales are: (a) 100 x 100 $Å^2$, (b) 200 x 200 $Å^2$, and (c) 400 x 400 $Å^2$. This series clearly shows the self-similarity of the sputtered surfaces over a wide range of length scales. Self-similarity was observed on all other sputtered graphite surfaces, one of which was etched at a faster rate than the sample shown here and the others at slower rates. The tunneling conditions were the same as those in Fig. 1.

It is also important to have a means of quantifying the surface morphologies produced by the sputter etching process. The patterns and scaling behavior of ion etched surfaces are extremely difficult to recognize directly from the experimental topographs, however. Fig. 3 shows a line scan image of the the last sputtered graphite surface studied. This data was acquired digitally in the constant current mode, which allows the heights of the surface features to be determined. After acquiring the data, the line scans were stored as a two dimensional array of heights, h(r). The bombardment conditions for this surface were the same as for the six other samples except that the total ion dose is lower (1.1 x 10^{17} ions/cm^2). It is possible to make **qualitative** comparisons of the topograph shown in Fig. 3 to computer simulations and other experimental scans but a different approach must be used to quantify this surface morphology. To make the data analysis quantitative, we utilize the two dimensional height-height correlation function:

$$G(|r_2-r_1|) = \langle h(r_1)h(r_2) \rangle - \langle h(r) \rangle^2,$$

where h(r) is the height of the surface at point $\mathbf{r} = (x,y)$ and < > denotes an average. A plot of G vs. surface separation length $|r_2-r_1|$ for this surface is shown in Fig. 4. G is calculated twice for the two dimensional data array h(r), once for the direction along the STM scan lines (G_x) and once for the direction perpendicular to the scan lines (G_y).

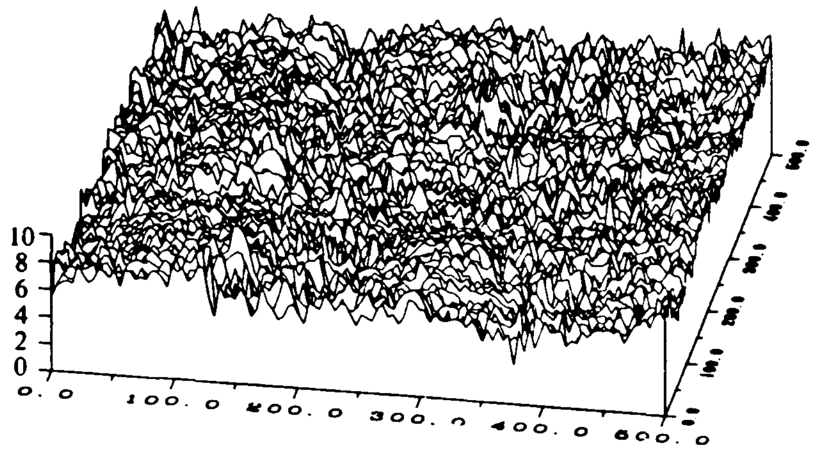

Fig. 3. Constant current topograph of a graphite surface that has been sputter etched with 5 keV Ar^+ ions. This sample was etched for 280 sec. with a beam current of 5.6 μA for a total dose of 1.1×10^{17} ions/cm^2. All distances are in Ångströms.

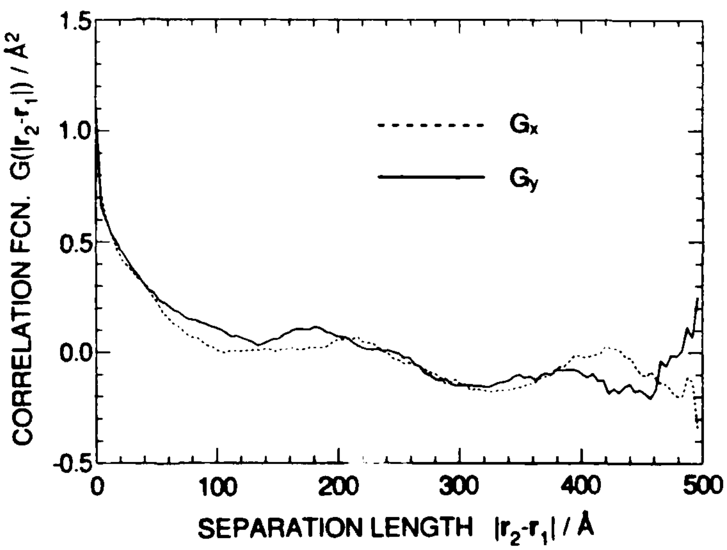

Fig. 4 Plot of the two dimensional height-height correlation function G vs. separation length for the sputtered graphite surface in Fig. 3. The scan size was 500 x 500 Å^2. The dashed curve shows G_x ; the solid curve is G_y . The fact that G > 0 for separation length > 0 indicates that the surface is not random and has a definite scaling behavior. As the separation length approaches 500 Å (the total scan width), G becomes unreliable due to poor statistics and edge effects of the STM scan.

The correlation function is a very useful form of data compression. First of all, the fact that G does not fall abruptly to zero for $|r_2-r_1| > 0$ indicates that there are indeed correlations on what may appear to be a completely random surface (note that $G(0) = (\langle h^2 \rangle - \langle h \rangle^2) > 0$). This is in agreement with the Shadow Model simulations for sputter etching, which produce mountain-like structures that are correlated for finite length scales. One potential problem for very rough surfaces is that the tunneling tip may not be able to exactly follow closely spaced surface features. The resulting topograph will then be a smoothed version of the true rough surface; the features will appear in the same place but the corrugations will be much smaller. This leads to artificially low values of the correlation function for small length scales and implies that we will always underestimate the correlation of closely spaced features. Another important property of the correlation function is that any difference between G_x and G_y indicates anisotropy on the surface, possibly produced by the directionality of the ion beam. The correlation function will be useful in future studies of the dependence of surface morphology on the ion beam incidence angle. It may also indicate anisotropy in the tunneling microscope scanning axes and can be a useful diagnostic when calibrating and tuning the instrument. Periodic structures on the surface will show up as a periodic signature in the correlation function. In Fig. 4, small peaks in G at separation lengths of approximately 200 Å and 400 Å indicate an underlying long range undulation of the surface of period ≈ 200 Å with many smaller features superimposed. Finally,the scaling behavior of the correlation function with separation length is important for making quantitative comparisons of computer simulations and experimental surfaces. Self-similar surfaces have correlation functions which follow a power law dependence, while a surface that appears smooth should show an exponential dependence of G with length.

CONCLUSIONS

In this study of the sputter etching process we have clearly demonstrated the usefulness of tunneling microscopy in topography investigations utilizing length scales larger than atomic dimensions. These measurements show a strong dependence of surface roughness on sputtering rate. In addition, images collected on different length scales show that each roughened surface is self-similar. These experimental observations agree qualitatively with computer simulations of ion beam sputter etching using the Shadow Model. The two dimensional height-height correlation function was used for quantifying surface topographies measured with the STM. Calculations of the correlation function show that these sputter etched surfaces are correlated for non-zero length scales and that they appear to have the same dependence on surface length scales as do the results of the computer simulations. Further STM studies of sputtering will focus on understanding both the macroscopic and microscopic topography of surfaces prepared by sputter erosion and on providing quantitative tests of theoretical work in this area.

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